Calibration of the graphite-methane buffer using the $f_{t_2}$ sensors at 2-kbar pressure

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Abstract

$H_2$ fugacities for the graphite-methane buffer assemblage in cold-seal pressure vessels have been measured at 2-kbar total pressure between 600 and 800°C using the Ag-AgBr-HBr and Ag-AgCl-HCl sensors with the previously calibrated Co-CoO-H_2O buffer as a reference. The measured $H_2$ fugacities of the buffer at temperatures between 650 and 800°C can be represented by

$$\log (f_{H_2})_{2 \text{ kbar}, T} (\pm 0.03) = 3.541 - 1675.9/T,$$

where $T$ is in kelvins. These $f_{H_2}$ values are about ¼ to ⅓ of the equilibrium values calculated from thermochemical data. These discrepancies may be attributed to the possibility that the $H_2$ fugacities generated in the pressure vessels from the decomposition of methane are not equilibrium values. However, it is also possible that the discrepancies were caused by errors in the thermochemical data and in the estimated fugacity coefficients of $H_2$ and $CH_4$ used in the equilibrium calculations. At temperatures below 650°C, reproducible steady-state $f_{H_2}$ values may not be established, and, therefore, this buffer technique should not be used. Also, in every laboratory, this buffer must be calibrated before it is applied to mineral-stability studies because the actual $H_2$ fugacities for this buffer may be system-dependent.

Introduction

The assemblage graphite + methane was first suggested by Eugster and Skippen (1967) as a possible $H_2$ buffer and has been used to study redox reaction equilibria by Skippen (1967), Rutherford (1969, 1973), Munoz and Ludington (1974), Hallam and Eugster (1976), and Popp et al. (1976). In these studies, samples were sealed in Pt or Ag-Pd capsules, which were permeable to $H_2$, and a constant $H_2$ fugacity was superimposed on these samples at constant pressure and temperature in a cold-seal pressure vessel by equilibrating the pressure-medium $CH_4$ with a graphite filler rod through the reaction

$$C_{(s)} + 2H_{2(g)} = CH_4(g).$$

(1)

The hydrogen fugacity values tabulated as a function of pressure and temperature by Skippen (1967, his Table 2) and Eugster and Skippen (1967, their Table 1) are calculated from thermochemical data. They extend from slightly higher than that of the fayalite-magnetite-quartz-2H_2O buffer at 450°C to that of the wüstite-magnetite-H_2O buffer at 825°C (see Rutherford, 1969, his Fig. 3; Eugster and Skippen, 1967, their Table 1). Applications of the graphite-methane buffer technique and also of its variations have been described by Huebner (1971).

Despite the wide application of the graphite-methane buffer in the past two decades, its $H_2$ fugacities have never been calibrated experimentally. In this study, the graphite-methane buffer was calibrated against the Co-CoO-H_2O buffer by using the $f_{H_2}$ sensor at 2 kbar and between 600 and 800°C. Preliminary results were presented earlier (Chou, 1980).

Experimental procedure

Preparation of $f_{H_2}$ sensors

The $f_{H_2}$ sensors consisted of sealed Pt capsules (1.85-mm OD, 1.54-mm ID, and 19-mm length) containing ~20-mg Ag, ~20-mg AgBr, and 15 to 20 μL of either distilled water (sensor A) or 1.5 M (molarity) HBr (sensor B). Details on the preparation, theory, and applications of a similar type of sensor, the Ag-AgCl-HCl type, have been presented elsewhere (Chou, 1978, 1987). Some sensors of the Ag-AgCl-HCl type were also used in this study to provide an independent check.

Experimental setup and sample analysis

The experimental setup is shown schematically in Figure 1. Each run consisted of four sensor capsules sealed, together with a graphite filler rod, in a conventional cold-seal pressure vessel (Tuttle, 1949). The pressure vessels were 3.18 cm in OD, 20.32 cm long, with a 6.35-mm bore, and were fabricated from Stellite 25 alloy. Matheson purity methane (±99.99% CH_4) was used as a pressure medium. To calibrate the graphite-methane buffer against the Co-CoO-H_2O buffer and to ensure the attainment of osmotic equilibrium, one sensor of type A and one of type B were exposed directly to the H_2-CH_4 atmosphere of the vessel, and one each of the types A and B sensors were enclosed in separated Au capsules (3.10-mm OD, 2.70-mm ID, and 25.4-
Fig. 1. Schematic diagram (not to scale) of the experimental setup.

mm length) containing the Co-CoO-H_2O H_2 buffer assemblage. Combining the sample (graphite-methane buffer) and the reference (Co-CoO-H_2O buffer) runs together in a single P-T experiment not only saves time and effort but also tends to cancel out any systematic errors in measurements of pressure and temperature. After pressurization and leak test, the pressure vessel-sample assemblage was heated in a horizontal tube furnace. Furnace temperatures were regulated by means of a solid-state temperature controller, and sample temperatures were measured by a conventional potentiometer using sheathed chromel-alumel thermocouples, which were calibrated against the melting points of NaCl (800.6°C), KCl (769.9°C), Al (659.9°C), and Zn (419.5°C) at 1 atm. The reported temperatures are estimated to be accurate to within ±5°C. A Heise gauge was used to monitor the pressure. Because the H_2 produced by the decomposition of CH_4 leaked continuously through the wall of the pressure vessel, CH_4 had to be replenished from time to time to maintain the total pressure. The maximum pressure drop was about 35 bars.

At the conclusion of each equilibration period, the pressure vessel-sample assemblage was quenched by a stream of compressed air. Capsules were removed, cleaned, and weighed. The sensor capsules were cleaned and pierced on a Teflon plate with a tungsten carbide needle. Between 5 and 10 μL of the solution were removed using a microcapacity disposable pipet, and bromide or chloride contents were then determined coulometrically with a Buchler Digital chloridometer. To ascertain that all solid buffer phases were present, the buffers were examined optically and/or by X-ray diffraction. In order to identify the nature of

Fig. 2. Experimental results from the Ag-AgBr-HBr sensors. Plotted are the data from Table 1. The arrows and chevrons represent data from sensors exposed to the graphite-methane buffer and the Co-CoO-H_2O buffer, respectively. Data from sensors A and B are represented by the symbols pointing up and down, respectively. Uncertainties are ±0.015 in log M_{Br} and ±5°C (shown by the lengths of the arrows and the horizontal bars; those associated with the chevrons are not shown for clarity). Experimental durations in days are given beside the arrows. Note that data for the Co-CoO-H_2O buffer are linear in the studied temperature range, but those for the graphite-methane buffer are linear only at higher temperatures. Lines drawn are least-squares fit of the data, excluding those at 600°C for the graphite-methane buffer. Note that data points for the graphite-methane buffer at 600°C are lower in M_{Br} than those for the Co-CoO-H_2O buffer.

Table 1. Experimental results from the Ag-AgBr-HBr hydrogen sensors at 2 kbar

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Pressure vessel no.</th>
<th>T (°C)</th>
<th>Duration (d)</th>
<th>Buffer</th>
<th>M_{Br} *</th>
<th>Log M_{Br}</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>15</td>
<td>804</td>
<td>2</td>
<td>Co-CoO</td>
<td>0.1613, 0.1611</td>
<td>-0.792, -0.793</td>
</tr>
<tr>
<td>16</td>
<td>13</td>
<td>751</td>
<td>2</td>
<td>C-CH_4</td>
<td>0.2293, 0.2276</td>
<td>-0.640, -0.643</td>
</tr>
<tr>
<td>18</td>
<td>13</td>
<td>744</td>
<td>2</td>
<td>Co-CoO</td>
<td>0.1445, 0.1384</td>
<td>-0.840, -0.859</td>
</tr>
<tr>
<td>14</td>
<td>13</td>
<td>706</td>
<td>2</td>
<td>C-CH_4</td>
<td>0.1961, 0.1968</td>
<td>-0.708, -0.706</td>
</tr>
<tr>
<td>12</td>
<td>13</td>
<td>658</td>
<td>3</td>
<td>Co-CoO</td>
<td>0.1224, 0.1316</td>
<td>-0.912, -0.881</td>
</tr>
<tr>
<td>9</td>
<td>13</td>
<td>650</td>
<td>9</td>
<td>C-CH_4</td>
<td>0.1889, 0.1881</td>
<td>-0.728, -0.726</td>
</tr>
<tr>
<td>11</td>
<td>15</td>
<td>604</td>
<td>3</td>
<td>Co-CoO</td>
<td>0.1081, 0.1058</td>
<td>-0.974, -0.976</td>
</tr>
<tr>
<td>15</td>
<td>15</td>
<td>603</td>
<td>7</td>
<td>Co-CoO</td>
<td>0.1426, 0.1411</td>
<td>-0.846, -0.851</td>
</tr>
</tbody>
</table>

* Molarities of Br^- measured coulometrically by a chloridometer. Two numbers are given for each buffer in each run; the first for sensor A and the second for sensor B.

** Sensor A leaked.
Table 2. $f_c$ values for the C-CH$_4$ buffer calibrated against those of the Co-CoO-H$_2$O buffer at 2-kbar total pressure

<table>
<thead>
<tr>
<th>Run no.</th>
<th>T (°C)</th>
<th>Log ($f_c$)$_{Co-CoO}$</th>
<th>Log $K_c$</th>
<th>Log $f_c$</th>
<th>Log ($f_c$)$_{Co-CoO}$</th>
<th>Log $f_c$</th>
<th>Log ($f_c$)$_{Co-CoO}$</th>
<th>Log $f_c$</th>
<th>Log ($f_c$)$_{Co-CoO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>804</td>
<td>-15.205</td>
<td>9.131</td>
<td>3.200</td>
<td>1.671</td>
<td>1.974</td>
<td>94.194</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>751</td>
<td>-17.448</td>
<td>10.335</td>
<td>3.133</td>
<td>1.521</td>
<td>1.861</td>
<td>72.630</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>744</td>
<td>-17.420</td>
<td>10.330</td>
<td>3.130</td>
<td>1.521</td>
<td>1.861</td>
<td>72.630</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>706</td>
<td>-18.719</td>
<td>11.016</td>
<td>3.088</td>
<td>1.431</td>
<td>1.685</td>
<td>48.373</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>658</td>
<td>-17.727</td>
<td>11.136</td>
<td>3.079</td>
<td>1.415</td>
<td>1.712</td>
<td>52.913</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>650</td>
<td>-16.943</td>
<td>11.129</td>
<td>3.071</td>
<td>1.415</td>
<td>1.712</td>
<td>52.913</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Calculated from log ($f_c$)$_{Co-CoO} = -24242.6/T + 7.205 + 0.052(P - 1)/T$, where $T$ is temperature in kelvins, and $P$ is pressure in bars (Chou, 1987).
** Equilibrium constant for the reaction H$_2$ + $\frac{1}{2}$O$_2$ = H$_2$O; interpolated from Robie et al. (1979).
† Calculated from log $f_c$ = log $f_c$ - log $K_c$ - $\frac{1}{2}$log $f_c$.
†† Calculated from Eq. 10; average values of $M_c$ from sensors A and B for each buffer were used in the calculation.

Calculations of hydrogen fugacities

For the reaction in the Ag-AgBr-HBr sensors at fixed $P$ and $T$, assuming pure solid Ag, $A_{G_{(Ag)}} + HBr_{(g)} = AgBr_{(s)} + \frac{1}{2}H_2(g)$

where $A_{AgBr}$ is the activity of AgBr in the liquid AgBr phase, and $f_{HBr}$ is the fugacity of HBr in the gas mixture at $P$ and $T$. Also,

$$f_{HBr} = f_{HBr}^* X_{HBr}$$

where $f_{HBr}^*$ is the fugacity of pure HBr at the same $P$ and $T$, $X_{HBr}$ is the activity coefficient of HBr in the mixture at $P$ and $T$ using pure HBr at the same $P$ and $T$ as the standard state, and $X_{HBr}$ is the molar fraction of HBr in the mixture.

Experimental result

The experimental results from the Ag-AgBr-HBr sensors are given in Table 1 and plotted in Figure 2. Hydrogen fugacities for the graphite-methane buffer calculated from these data are tabulated in Table 2. Results from the Ag-AgCl-HCl sensors are given in Table 3.

Calculations of hydrogen fugacities

For the reaction in the Ag-AgBr-HBr sensors at fixed $P$ and $T$, assuming pure solid Ag,
\[ X_{\text{HBr}} = \frac{m_{\text{HBr}}}{(m_{\text{H}_2O} + m_{\text{HBr}} + m_{\text{H}_2} + m_{\text{Br}_2} + m_{\text{O}_2})}, \]

where \( m_i \) is molality of \( i \) at \( P \) and \( T \).

Combining Equations 3, 4, and 5, we have

\[ (f_{\text{H}_2})_{P,T} = \left[ \frac{(K_{\text{HBr}}^*)}{(a_{\text{AgBr}})_{1,M}} \right]_{P,T} (m_{\text{HBr}})_{P,T}, \]

where \( i \) includes \( \text{H}_2, \text{H}_2O, \text{HBr}, \text{Br}_2, \) and \( \text{O}_2, \) and \( m_{\text{HBr}} \) is the molality of associated \( \text{HBr} \) at \( P \) and \( T \). At 2-kbar total pressure, according to the ionization-constant data of \( \text{HBr} \) (Quist and Marshall, 1968), more than 91% and 97% of total \( \text{Br} \) \( (m_{\text{Br}_2} + m_{\text{Br}_2}) \) at, respectively, 600 and 650°C are associated. Therefore,

\[ (m_{\text{Br}_2})_{\text{dissolved}} = (m_{\text{Br}_2})_{P,T,25^\circ C} \]

Osmotic equilibrium can be demonstrated by attaining reversibility in the flow of \( \text{H}_2 \) (Shaw, 1967, p. 529). For the system approaches equilibrium, \( \text{H}_2 \) in the outer system diffuses into sensor A and reacts with \( \text{AgBr} \) forming \( \text{HBr} \), while \( \text{HBr} \) in sensor B reacts with \( \text{Ag} \) producing \( \text{AgBr} \) and \( \text{H}_2 \) which diffuses out of sensor B into the outer system. The same value for \( (m_{\text{Br}_2})_{\text{dissolved}} \) in sensors A and B in each run indicates that the system has reached osmotic equilibrium, and the \( f_{\text{H}_2} \) obtained from the \( (m_{\text{Br}_2})_{\text{dissolved}} \) value measured in the sensors and calculated from Equation 9 reflects \( f_{\text{H}_2} \) of the outer system. Two kinds of outer systems were used in this study to superimpose constant \( /\text{H}_2 \) values in each run: one by the graphite-methane \((\text{C}-\text{CH}_4)\) buffer and the other by the \( \text{Co-CoO}-\text{H}_2 \text{O} \) buffer (see Fig. 1). According to Equation 9, these two \( f_{\text{H}_2} \) values are related by

\[ (f_{\text{H}_2})_{\text{C-CH}_4} = (f_{\text{H}_2})_{\text{Co-CoO}} \left( \frac{m_{\text{H}_2\text{O}^\text{C-H}_2}}{m_{\text{H}_2\text{O}^\text{Co-CoO}}} \right)_{\text{dissolved}}. \]

Results are given in Table 3 and plotted in Figure 3 (shaded boxes).

**Discussion**

\( \text{H}_2 \) fugacities of the graphite-methane buffer measured by means of the \( \text{Ag-AgBr}-\text{HBr} \) sensors and by means of the \( \text{Ag-AgCl-HCl} \) sensors (Table 4) because molality and molarity units for a concentrated \( \text{Cl}^- \) solution are somewhat different, as shown in Table 3. Consequently, Equation 10 becomes

\[ (f_{\text{H}_2})_{\text{c-CH}_4} = (f_{\text{H}_2})_{\text{e-CH}_4} \left( \frac{m_{\text{H}_2\text{O}^\text{C-CH}_4}}{m_{\text{H}_2\text{O}^\text{Co-CoO}}} \right)_{\text{dissolved}}. \]

**Discussion**

\( \text{H}_2 \) fugacities of the graphite-methane buffer measured by means of the \( \text{Ag-AgBr}-\text{HBr} \) and \( \text{Ag-AgCl-HCl} \) sensors at temperatures between 650 and 804°C can be represented by the equation

\[ \log (f_{\text{H}_2})_{\text{c-CH}_4} = 3.541 - 1675.9 / T \]

where \( T \) is temperature in kelvins. Equation 14 is the least-squares fit of the data given in Tables 2 and 3, and is shown in Figure 3. The coefficient of determination \( r^2 = 0.890 \). These measured \( \text{H}_2 \) fugacities are about \( 1/4 \) of the equilibrium values calculated from thermochemical data (Eugster and Skippen, 1967). These discrepancies are too large to be totally attributed to the uncertainties associated with the \( \text{Co-CoO} \) buffer; when the \( \text{Co-CoO} \)}
buffer data reported by Myers and Gunter (1979) (also Fig. 3) are used in Equations 10 and 13, the \((f_{H_2})_{C-CH_4}\) values reported in Table 2 are only, respectively, 4.48, 10.56, and 3.26 bars higher at 804, 706, and 604°C. However, the discrepancies between the calculated and the measured \(H_2\) fugacities may be attributed to (1) the errors in the thermochemical data and in the estimated fugacity coefficients of \(H_2\) and \(CH_4\) used in the calculations, and/or (2) the nonequilibrium nature of the measured \(H_2\) fugacities. The reasons for (2) are (a) the buffer reaction (Eq. 1) was calibrated in the direction of \(H_2\) generation only, and the reversal of the reaction was not demonstrated; (b) the X-ray diffraction data show that carbon produced by the decomposition of methane was amorphous instead of crystalline graphite (the former had a higher carbon activity that resulted in a lower \(f_{H_2}\), as observed); (c) a continuous leakage of \(H_2\) from the pressure vessels was indicated by the continuous total pressure drop during the run; and (d) the buffer system was contaminated by the pressure-vessel material as indicted by the presence of \(Ni\), \(C\) (\(x > 4\)) and \(WC\) as reaction products. \(Ni\), \(C\) and \(WC\) were examined optically and by means of the X-ray diffraction. \(Ni\), \(C\) was identified by its (111), (200), and (022) peaks (Pugh et al., 1961), and \(WC\) by its (001), (100), and (101) peaks (Goldschmidt, 1949). \(Ni\) and \(W\) came from the Stellite 25 pressure vessels, which consisted mainly of \(Co\) (\(50-55\) wt%), \(Cr\) (\(20\)%), \(W\) (\(15\)%), \(Ni\) (\(10\)%), and \(Fe\) (\(3\)%).

Even though equilibrium \(H_2\) fugacities for the graphite-methane buffer may not be obtained in the pressure vessels, steady-state values can be established through two counteracting processes: steady generation of \(H_2\) by decomposition of methane and steady loss of \(H_2\) by diffusion through the pressure vessel wall. The \(f_{H_2}\) values measured by using the \(Ag-AgCl-HCl\) and \(Ag-AgBr-HBr\) sensors at 2-kbar total pressure and at \(\sim 650\) and \(\sim 600°C\) are compared in Figure 4 as a function of experimental duration. In order to minimize the difference in their physical setup, the same pressure vessel-furnace assembly was used for all runs in each temperature set. At \(\sim 650°C\), \(f_{H_2}\) values of the graphite-methane buffer measured by means of the two types of sensors converge in about 3 d. Those at \(\sim 600°C\) do not converge at all, even though each system in which the same kinds of sensors are used tends to establish its own quasi-steady-state \(f_{H_2}\); the quasi-steady-state \(f_{H_2}\) values measured by the \(Ag-AgCl-HCl\) sensors are more than two times higher than those determined by the \(Ag-AgBr-HBr\) sensors. This discrepancy cannot be attributed to the uncertainties in pressure, temperature, and chemical analysis, because each run has its own \(Co-CoO-H_2O\) buffer reference, which behaves normally as indicated by the linear relation of the data in the \(log M_{H_2} vs. 1/T\) plot shown in Figure 2. However, it is possible that at \(\sim 600°C\), the rate of \(H_2\) generation in Reaction 1 is so sluggish that the steady-state \(f_{H_2}\) of the system is not controlled by this reaction but rather by the budget of \(H_2\) in the system, with the sensors attempting to control \(f_{H_2}\). The other \(H_2\)-generating reaction in the system is not controlled by this reaction but rather by the budget of \(H_2\) in the system, with the sensors attempting to control \(f_{H_2}\).

Because the steady-state \(H_2\) fugacities approximated by Equation 14 may not be the equilibrium values for the graphite-methane buffer, and also because the permeation rates of \(H_2\) through the pressure-vessel walls depend on the material, dimension, and history of usage of the pressure vessels, this buffer must be calibrated in every laboratory before it can be applied in redox-controlled studies. Also, the graphite-methane buffer should not be used at temperatures below \(650°C\), because reproducible steady-state \(H_2\) fugacities may not be established at these low temperatures.

**Conclusions**

The \(H_2\) fugacities for the graphite-methane buffer have been calibrated at 2-kbar total pressure against the previously calibrated \(Co-CoO-H_2O\) buffer between 600 and \(800°C\). At temperatures below \(650°C\), reproducible steady-state \(f_{H_2}\) may not be established, probably because of the sluggish nature of the decomposition reaction of \(CH_4\) in Reaction 1. However, at higher temperatures, steady-state \(f_{H_2}\) can be established and maintained. The graphite-methane buffer must be calibrated in every laboratory before it can be used in mineral stability studies, because the steady-state \(f_{H_2}\) values approximated from Equation 14 may not represent equilibrium values and the actual \(f_{H_2}\) values of this buffer may be system-dependent.

*Note added in proof.* The discrepancies between the calculated and measured \(f_{H_2}\) values for the \(C-CH_4\) buffer (see Fig. 3) can be partially attributed to the possible nonequilibrium nature of the measured \(M_{H_2}\) and \(M_{CH_4}\) values in the \(f_{H_2}\) sensors exposed to the \(Co-CoO-H_2O\) buffer; those concentrations listed in Tables 1 and 3 (except run nos.
11 and 15) are probably higher than their respective equilibrium values owing to the relatively high flux of H$_2$ into the Au capsules coupled with the sluggishness of the buffer reaction (CoO + H$_2$ $\rightarrow$ Co + H$_2$O).

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